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(54) Curable composition.

(57) Compositions curable upon exposure to atmospheric
moisture at room temperature comprising (a) organic
polymer having at least one hydrolyzable silicon-containing
group in the molecule and having a molecular weight from
about 500 to 15,000, and (b) a photocurable substance.

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Curable Composition

1 This invention relates to a curable composition comprising a polymer having a hydrolyzable silicon containing group, which is curable to a rubber-like substance upon exposure to atmospheric moisture at room temperature.

5 The above type of composition finds many applications, for example, as a sealant or adhesive used for building construction. Important characteristics required for this type of composition are, among others, residual tack and weather-durability of adhesive force after application. These characteristics are directly related to the deposition of dust particles on the resulting sealant surfaces and the adhesive force with glass. In U.S. Patent 3,971,751 assigned to the same assignee as the present application, there is shown a curable composition comprising a polyether having a hydrolyzable silicon containing group, which exhibits good mechanical properties such as strength, elongation, adhesion and the like. Similar polymeric compositions having a hydrolyzable silicon containing group include those described in U.S. Patent 3,408,321, 3,592,795 and 3,632,557. Experience has shown, however, that these curable compositions are not satisfactory in residual tack and weather-durability of adhesive force.

10 15 20 25

According to the present invention, we have found that the foregoing and other disadvantages may be overcome by compounding

(a) about 100 parts by weight of an organic polymer having

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- 1 at least one hydrolyzable silicon-containing group in the
molecule and having a molecular weight from about 500 to
15,000, and
5 (b) about 0.01 to 30 parts by weight of a photocurable sub-
stance. The resulting mixture becomes tack-free very shortly
and retains its maximum adhesive force upon exposure to light
for a long time.

The photocurable substance will react only in those
areas which are exposed to light such as the exterior surface
10 or interface of sealant with glass, to improve the tack-free
time and photo-durability in these areas without affecting on
other properties of the sealant such as strength, elongation
or the like.

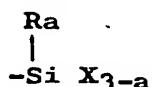
The term "photocurable substance" used herein designates
15 those substances which are capable of photopolymerization or
photocrosslinking to produce an insoluble mass. Several types
of photocurable substance are known in the art including
acrylic or methacrylic monomers and oligomers, polyvinylcin-
namate and organic azide group-containing material. Photocur-
20 able acrylic or methacrylic monomers and oligomers are acrylic
or methacrylic esters, preferably esters of a polyhydric
aliphatic alcohol with acrylic or methacrylic acid having at
least two ester linkages in the molecule. Examples of these
esters include diethyleneglycol diacrylate, polyethyleneglycol
25 diacrylate, neopentylglycol diacrylate, 1,5-pentanediol
diacrylate, 1,6-hexanediol diacrylate, trimethylolpropane

1 triacrylate and the corresponding methacrylates. Mixtures of
these monomers and oligomers may also be used.

Polyvinyl cinnamate may be produced by acylating polyvinyl
alcohol with, for example, cinnamoyl chloride. Derivatives
5 of polyvinylcinnamate such as mixed ester with dibasic car-
boxylic acid may also be used.

Examples of organic azide group-containing material
include azidized natural or synthetic rubber and azide group-
containing polyorganosiloxanes as shown in Japanese Laying
10 Open Patent Application 30250/79.

The polymers having hydrolyzable silicon-containing group
which may be used in the present invention include those
described in the above-cited patents. Preferably they have
a polyether or polyester main chain having a molecular weight
15 of about 500 to about 15,000 and are each terminated with at
least one hydrolyzable group of the formula:



wherein R is a hydrocarbon group of 1 to 20 carbon atoms, X
is a hydrolyzable group such as C₁-C₁₀ alkoxy group, aminoxy
group or the like, and a is 0, 1 or 2,

20 About 0.01 to about 30 parts by weight of said photocur-
able substance may be incorporated to 100 parts by weight of
said hydrolyzable group-containing polymer. A proportion of
said photocurable substance less than 0.01 parts cannot ex-
hibit the desired effect to the fullest extent, while excessive

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1 use thereof may adversely affect on the properties of resulting sealant.

5 The curable composition of the present invention may contain plasticizers such as dioctylphthalate, epoxylated soybean oil or the like, fillers such as calcium carbonate talc or the like, pigments such as titanium dioxide, carbon black or the like, thixotropic agents such as hydrogenated castor oil, anti-aging agents such as UV-absorbants or free radical initiation inhibitors, and other conventional ingredients.

10 The curable composition of the present invention may be prepared by kneading or milling the foregoing components on a conventional kneader or paint rollers. When one component composition is desired, the composition is completely dehydrated after the addition of a curing agent. If desired, the 15 curing agent may be stored and shipped in a separate container and mixed with the curable composition *in situ* before use.

20 Examples of curing agent which may be employed in the present invention include tin compounds such as stannous 2-ethylhexanate, dibutyltindilaurate, lead compounds such as lead 2-ethylhexanate, iron compounds such as iron naphthenate, amines such as laurylamine, basic compound such as active zinc white, carboxylic acids such as capric acid, alkyl titanates, organosilicon titanates or the like. Mixtures of these agents 25 may be also used. The curing agent can be used in amounts from about 0.001 to 10 parts by weight per 100 parts by weight

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1 of hydrolyzable group-containing polymer.

The following examples are given by way of illustration and not by way of limitation. All parts are by weight.

Example 1

5 To 100 parts of a polyoxypropylene having an average molecular weight of 8,000 and terminal groups of the formula:

$$\begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_3\text{O})_2\text{Si}- \end{array}$$
 at a proportion of about 80% were added 5 parts of a polyfunctional acrylate (trimethylolpropane triacrylate, sold by Toagosei Chemical Industry Co., Ltd., Tokyo, under the name of ARONIX M-109), 30 parts of dioctyl phthalate, 100 parts of calcium carbonate, 25 parts of titanium dioxide, 3 parts of hydrogenated castor oil and 1 part of styrenated phenol. The mixture was mixed with a lancet and then intimately milled by passing through a 3-roll paint mil three times.

15 To 264 parts of the resulting mixture were added 1 part of stannous 2-ethylhexanate and 1 part of laurylamine. The mixture was then poured onto a glass plate and allowed to cure under atmospheric conditions while exposing to light. After 7 days, the resulting cured sheet showed no residual tack by a finger test. The sheet did not peel off from the interface with glass plate by pulling an edge by hand after exposing to light for 60 days. A control having similar composition but not containing ARONIX M-109 showed residual

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1 tack and peeled off in the same tests.

Example 2

To 100 parts of a polyoxypropylene having an average molecular weight of 9,000 and terminal groups of the formula:

5
$$\begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_3\text{O})_2\text{Si}- \end{array}$$
 at a proportion of about 90% were added 10 parts of polyvinyl cinnamate, 30 parts of triethyleneglycol diacetate, 100 parts of calcium carbonate, 25 parts of titanium dioxide, 3 parts of hydrogenated castor oil and 1 part of styrenated phenol.

10 The mixture was mixed with a lancet and then intimately milled by passing through a 3-roll paint mil three times.

To 269 parts of the resulting mixture were added 1 part of stannous 2-ethylhexanate and 1 part of monoethanolamine. The mixture was then dehydrated in vacuo with stirring in a vacuum kneader. The curable composition thus obtained was applied onto outdoor building construction as a sealant. The cured product showed no residual tack after 7 days and had weather-proof adhesion property.

Example 3

20 To 100 parts of a polyoxypropylene having an average molecular weight of 9,000 and terminal groups of the formula:

$$\begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_3\text{O})_2\text{Si}- \end{array}$$
 at a proportion of about 85% were added 5 parts of azidized natural rubber, 30 parts of diamylphthalate,

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1 150 parts of calcium carbonate and 1 part of styrenated
phenol. The mixture was mixed with a lancet and intimated
milled by passing through a 3-roll paint mil three times.

5 To 286 parts of the resulting mixture were added 2 parts
of dibutyltindilaurate and 3 parts of active zinc white and
the mixture was thoroughly mixed. The resulting composition
was applied onto outdoor construction. The cured product
showed no residual tack after 7 days and had weather-proof
adhesion property.

10 The above has been offered for illustrative purposes
only, and it is not for the purpose of limiting the scope of
this invention, which is as defined in the claims below.

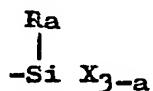
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1 WE CLAIM:

1. A curable composition comprising

- (a) about 100 parts by weight of an organic polymer having at least one hydrolyzable silicon-containing group in the molecule and having a molecular weight from about 500 to 15,000, and
(b) about 0.01 to 30 parts by weight of a photocurable substance.

2. The composition according to Claim 1, wherein said hydrolyzable silicon-containing group is a group of the formula:

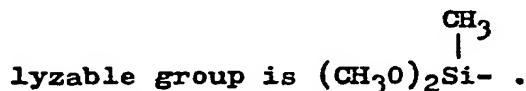


wherein R is a hydrocarbon group of 1 to 20 carbon atoms, X is a hydrolyzable group, and a is 0, 1 or 2.

3. The composition according to Claim 2, wherein said hydrolyzable group is C₁-C₁₀ alkoxy or aminoxy group.

15 4. The composition according to Claim 1, wherein said organic polymer has a polyether main chain.

5. The composition according to Claim 4, wherein said hydro-



20 6. The composition according to Claim 1, wherein said photocurable substance is selected from the group consisting of

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1 acrylic or methacrylic monomers and oligomers, polyvinyl-
cinnamate, and organic azide group-containing material.

7. The composition according to Claim 4, wherein said photo-
curable substance is an ester of acrylic acid with a poly-
5 hydric alcohol having at least two ester linkages in the
molecule.

8. The composition according to Claim 4, wherein said photo-
curable substance is polyvinylcinnamate.

9. The composition according to Claim 4, wherein said photo-
10 curable substance is azidized natural rubber.

10. The composition according to Claim 4, further comprising
in one component composition a curing agent selected from
the group consisting of an organic tin compound, an organic
lead compound, organic iron compound, an amine, a carboxylic
15 acid, zinc white, alkyl titanate and organosilicon titanat .

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 80101117.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
A, D	<p><u>US - A - 3 971 751</u> (K.ISAYAMA et al.) + Totality + --</p>	1-5,10	C O8 L 101/02/ C O9 K 3/10 (C O8 L 101/02 C O8 J 3/24 C O8 L 71/02)		
A	<p><u>DE - B - 1 794 028</u> (DOW CORNING LTD.) + Claims 1,3,4; examples 7,8 + -----</p>	1-3,5, 10			
<table border="1"> <thead> <tr> <th>TECHNICAL FIELDS SEARCHED (Int.Cl.3)</th> </tr> </thead> <tbody> <tr> <td>C O8 L 101/00 C O8 L 71/00 C O8 J C O8 G 85/00 C O9 K C O8 G 65/00</td> </tr> </tbody> </table>				TECHNICAL FIELDS SEARCHED (Int.Cl.3)	C O8 L 101/00 C O8 L 71/00 C O8 J C O8 G 85/00 C O9 K C O8 G 65/00
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<table border="1"> <thead> <tr> <th>B: member of the same patent family, corresponding document</th> </tr> </thead> </table>				B: member of the same patent family, corresponding document	
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Date of completion of the search	Date of completion of the search	Examiner			
28-10-1980	28-10-1980	KALTENECKER			
The present search report has been drawn up for all claims					
28-10-1980	28-10-1980	Examiner			
VIENNA	28-10-1980	KALTENECKER			